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Electron Attachment and Molecular Fragmentation in Laser-Excited Plasmas

FINAL REPORT

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Production of O^{-} from thermal electrons has been identified during the laser excitation of NO. O^{-} is produced during excitation near 226 nm, corresponding to absorption in the (0,0) band of the A - X band system of NO Electrons with energy limited to <0.5 eV completely suppress the endothermic production of O^{-} from NO($X^2\Pi$). Dissociative attachment occurs from the $A^2\Sigma^+$ electronic state of NO and produces both O^{-} and N in their ground electronic states. This is the first reported case of dissociative attachment of electrons to an optically prepared excited electronic state. Keywords

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Research Problem

The central aim of this project has been the detailed understanding of the dissociative electron capture by excited electronic states of isolated small molecules under nearly collision-free conditions. To this end, we have studied the dissociative capture of thermal electrons by the thoroughly documented $A^2\Sigma^+$ electronic state of nitric oxide, NO, a process which is highly endothermic for the ground $X^2\Pi$ state of that molecule.

Major Results

Production of O^- from thermal electrons has been identified during the laser excitation of nitric oxide at low pressure. The O^- ion is produced during excitation near 226 nm, corresponding to absorption in the (0,0) band of the $A^2\Sigma^+ - X^2\Pi$ band system of NO. An electron gun provides electrons with energy limited to <0.5 eV kinetic energy, completely suppressing the highly endothermic production of O^- from NO($X^2\Pi$). From basic thermodynamic considerations, we conclude that dissociative attachment occurs from the $A^2\Sigma^+$ electronic state of NO, proceeds through predissociation of the $^3\Sigma^+$ excited state of NO^-, and produces both O^- and N in their ground electronic states. This is the first reported case of dissociative attachment of electrons to an optically prepared excited electronic state under collision-free conditions.

The process responsible for producing O^- may be written:

$$NO^* (A^2\Sigma^+) + e \rightarrow O^-(^2P) + N(^4S) \qquad (1)$$

The ability to identify this process definitively allows us to interpret much of the previous data we have acquired regarding laser-enhanced production of negative ions. No rotational dependence of the dissociative attachment cross-section has been observed, consistent with the identification of the attaching state as a Rydberg state exhibiting Hund's case d coupling.

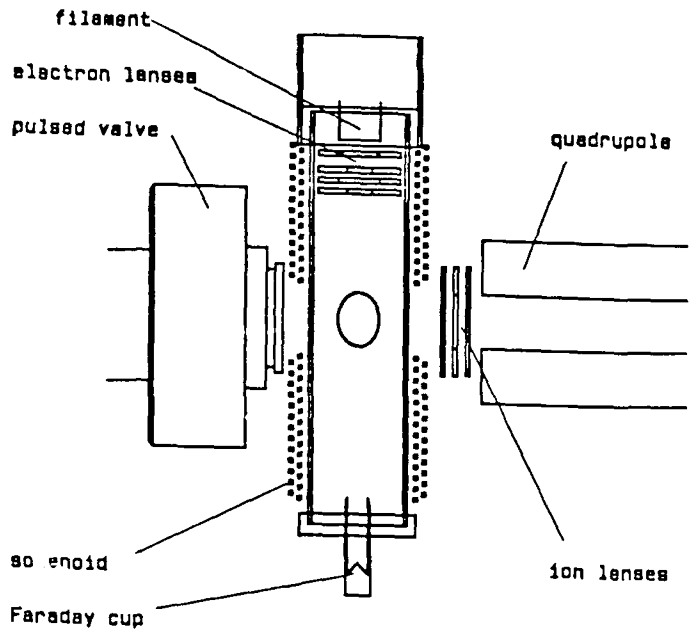
We have further characterized the dissociative attachment of thermal electrons to the $A^2\Sigma^+$ state of NO by calibrating the response of our detection system to dissociative attachment processes of known cross-section. By measuring the attachment of thermal electrons to carbon tetrachloride in our experimental apparatus, we are able to calibrate the response of our mass-analyzed detection system at mass 35, and measuring of the attachment of electrons at various energies to SO_2 allows us to calibrate the relative throughput of our mass analyzer at masses 16, 32, and 48. The resulting information allows us to estimate an absolute cross-section of approximately 10^{-16} cm^2 for the attachment of thermal electrons to NO $(A^2\Sigma^+, v=0)$, compared with a maximum cross-section for the ground

state of 10^{-18} cm^2 at 8.1 eV.

The experimental arrangement is illustrated in Fig. 1. The apparatus is designed to monitor the ions produced when a pulsed molecular beam is allowed to interact simultaneously with a beam of low energy electrons and radiation from a pulsed tunable dye laser. About 10 mm downstream of the nozzle admitting the sample, the gas interacts with laser radiation and low energy electrons in a low pressure reaction region at a constant electric potential. Ions produced from dissociative attachment are focused using a three-cylinder electrostatic ion lens, mass selected using a quadrupole mass filter, and detected with an electron multiplier.

The sample of pure NO is introduced to the vacuum chamber using a pulsed valve (Lasertechnics 203LPV) with a 1 mm diameter aperture at a stagnation pressure of 100 Torr. The chamber is evacuated using a 6 inch oil diffusion pump with a refrigerated baffle. The pulse rate is adjusted to maintain the background pressure in the chamber to $<10^{-7}$ Torr, during the opening of the pulsed valve, the pressure in the detection region typically rises to $5 \cdot 10^{-7}$ Torr.

Fig. 1. The experimental apparatus used in the dissociative attachment studies of NO.



Spectra were recorded using a frequency-doubled tunable dye laser (Lambda Physik FL 2002) pumped by a XeCl excimer laser operating at 308 nm (Lambda Physik EMG 150). The dye used was Coumarin 450; the output of this dye was doubled using an angle tuned extracavity KDP doubling crystal to a wavelength between 227 and 225 nm. Care was taken to limit the laser power incident on the sample so as to eliminate the production of photoelectrons from the multiphoton ionization of NO; the laser was loosely focused into the sample chamber using either a long focal length lens or a reducing telescope, and the total power was further reduced using a series of quartz plates until neither photoelectrons nor positive ions were detected.

The source of low-energy electrons is an electron gun based on the design of Orient and Srivastava. Thermionic emission from a tungsten filament is focused with a set of cylindrical electrostatic lenses and monitored with a Faraday cup. The energy of the electrons is controlled by changing the bias on the filament with respect to ground; the electron energy was calibrated by monitoring the energy required for dissociative attachment to SO_2 and NO. Electrons are confined to the interaction region by a weak magnetic field (flux density ~ 150 Gauss) produced with a small solenoid surrounding this region. This technique, sometimes referred to as momentum filtering, is capable of preventing the electrons from leaving the interaction region while allowing the more massive charged particles to pass through unimpeded. This arrangement allows us to record a relatively weak signal from negatively charged ions without interference from the much more numerous electrons. At an electron energy of ~0.2 eV, this device produces an electron current at the Faraday cup of 30 picoamperes.

Current from the electron multiplier was measured using a gated integrator, and the output from the gated integrator was digitized and stored by a microcomputer for subsequent display and analysis. The same microcomputer also supervised other aspects of data ac-

quisition such as tuning the dye laser and doubling crystal, opening the gas nozzle, and firing the excimer laser.

The dissociative attachment of electrons to NO under these conditions is highly dependent on laser irradiation, producing a signal which follows the known absorption spectrum of NO to within experimental error, as shown in Fig. 2. The conclusion that electrons are

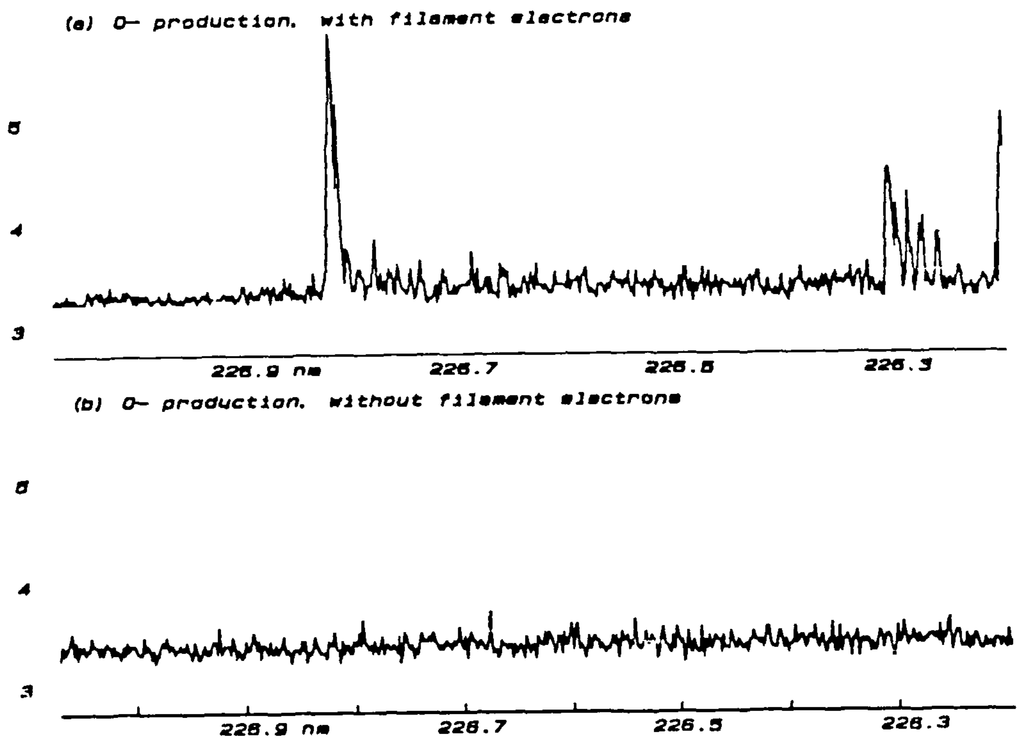


Figure 2. The photoenhanced attachment spectrum of NO, showing production of mass-resolved O^- ions as a function of laser wavelength (in nm). Spectrum (a) was taken in the presence of a current of ~30 picoamperes of electrons from an electron gun at an energy of ~0.2 eV; spectrum (b) shows the base line observed without the electron current. The two band heads in spectrum (a) are the P_1 and P_2 heads in the (0,0) band of the A-X system of neutral NO.

being attached to the $A^2\Sigma^+$ state is inescapable. This result opens the possibility of controling the conductivity of a diffuse discharge containing NO or other small molecules optically, which was one of the major motivations of this work. In addition, it may provide enhanced understanding of other laser-mediated processes such as optogalvanic effects and laser-excited photochemistry.

This technique offers a potential method for studying the dissociative attachment of electrons to small molecules in rovibonically selected states. Such studies are, in principle, capable of probing the dissociative potential functions of the negative ion. Inasmuch as there are few experimental techniques for exploring these excited potential curves, the information gained would be unique.

In other work, we have observed an extremely unusual pattern of fragmentation of molecular chlorine by collisions with species in a helium plasma. The products of this fragmentation are chlorine atomic ions which are very highly excited both electronically and translationally. The only plausible mechanism which reproduces the observations involves simultaneous charge and energy transfer from an excited helium ion to Cl_2, producing Cl_2^{+2}, which promptly dissociates into highly excited atomic ions. In addition to enhancing our

understanding of the physics of dissociative charge transfer, identification of this unexpected process may prove important to applications which involve chemical plasma etching by helium/chlorine plasmas and may provide a mass spectrometric diagnostic tool (involving coincidence measurement of Cl^+ pairs) for detection of metastable He^+.

Further characterization of the helium-chlorine plasma has led to an assignment of the Λ-type doubling in the $A^2\Pi_u$-$X^2\Pi_g$ band system of Cl_2^+ (Fig. 3). Several bands of the A-X emission spectrum of Cl_2^+ have been recorded at high resolution in a rotationally cold supersonic expansion of Cl_2 and He excited with a corona

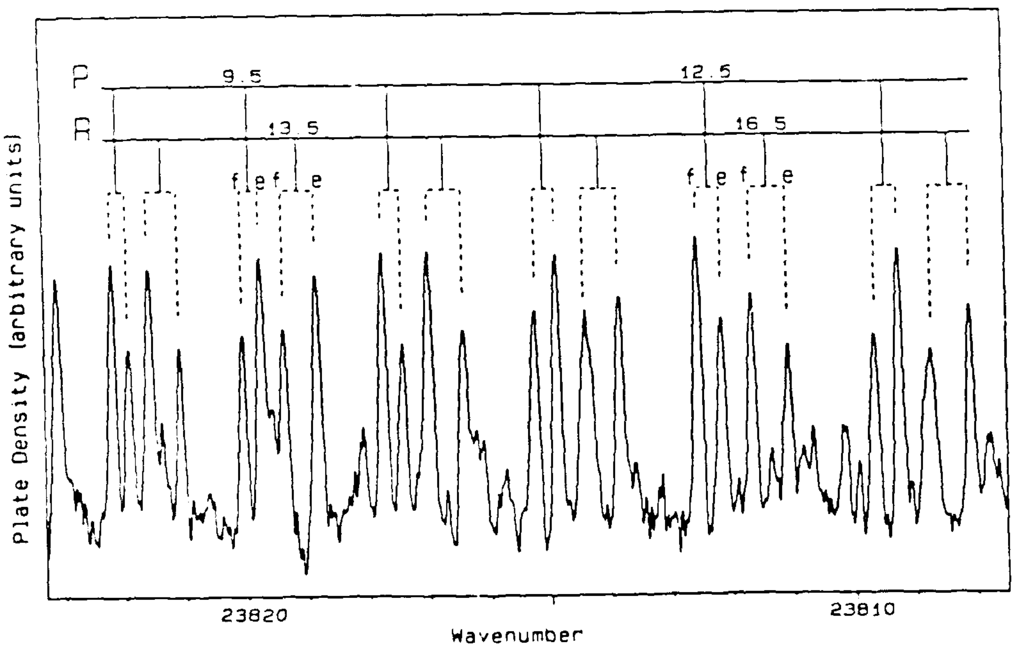


Fig. 3. A part of the near-ultraviolet spectrum of Cl_2^+, showing resolution of the Λ-doubling components of the rotational fine structure.

discharge. The Λ-type doubling has been observed for the first time in this system, confirming the identity of these bands as members of the $\Omega=\frac{1}{2}$ component of the electronic transition. Rotational constants have been obtained with higher precision than has previously been possible, allowing us to clarify some outstanding questions about the relative vibrational numbering of these bands. This assignment allows the first estimates of the importance of the nearby $^2\Sigma^+_u$ state of that molecule and may enable a deperturbation of the exceedingly complicated physics of the upper state.

PUBLICATIONS

The following refereed articles were published during the current funding period:

"Dissociative Attachment of Electrons to the $A^2\Sigma^+$ State of Nitric Oxide," C.-T. Kuo, Y. Ono, J. L. Hardwick, and J. T. Moseley, J. Phys. Chem. 92, 5072 (1988).

"Λ-Doubling in the Jet-Cooled A-X Emission Spectrum of Cl_2^+," J. C. Choi and J. L. Hardwick, J. Mol. Spectrosc., accepted for publication.

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